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NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To:

Assistant Commissioner for Patents
United States Patent and Trademark Office
Box PCT
Washington, D.C.20231
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 06 September 2000 (06.09.00)	
International application No. PCT/US00/01160	**Applicant's or agent's file reference** CL1330PCT
International filing date (day/month/year) 19 January 2000 (19.01.00)	**Priority date** (day/month/year) 25 January 1999 (25.01.99)
Applicant O'BRIEN, John, P.	

1. The designated Office is hereby notified of its election made:

[X] in the demand filed with the International Preliminary Examining Authority on:

27 July 2000 (27.07.00)

[ ] in a notice effecting later election filed with the International Bureau on:

2. The election [X] was

[ ] was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

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INTERNATIONAL SEARCH REPORT

PTO/PCT Rec'd 05 JUN2001

International application No.
PCT/US99/01860

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C12P 19/02, 19/04 ; C12M 1/00
US CL :435/101, 283.1

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 435/101, 283.1

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X - A	US 4,356,262 A (HEADY) 26 October 1982, see col 1, l 29-45 in particular.	1-4, 7, 13-19, 21 --- 5-6, 8-12
X	US 4,533,633 A (WEIDENBACH et al) 06 August 1985, see Figure 3, containing an inlet and outlet tube and enyzme.	22-30
X	US 4,956,289 A (WRASIDLO et al) 11 September 1990, see Figures 1-4, which discloses an inlet and outlet reactor vessel and an enzyme.	22-30
X - Y	US 5,141,858 A (PAUL et al) 25 August 1992, see column 2, lines 47-52 in particular.	13-19 --- 20

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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Date of the actual completion of the international search 22 MARCH 1999	Date of mailing of the international search report 14 APR 1999
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer DR. HERBERT J. LILLING Telephone No. (703) 308-0196

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PATENT COOPERATION TREATY

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INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference	**FOR FURTHER ACTION** see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
CL1330PCT		
International application No.	International filing date *(day/month/year)*	(Earliest) Priority Date *(day/month/year)*
PCT/US 00/01160	19/01/2000	25/01/1999
Applicant		
E.I. DU PONT DE NEMOURS AND COMPANY		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 03 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**

   a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

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3. [ ] **Unity of invention is lacking** (see Box II).

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6. The figure of the **drawings** to be published with the abstract is Figure No. 1

   [X] as suggested by the applicant.

   [ ] None of the figures.

   [ ] because the applicant failed to suggest a figure.

   [ ] because this figure better characterizes the invention.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/IS 00/01160

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 D01F9/00 C08L5/00 C12P19/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
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Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 501 886 A (O'BRIEN JOHN P) 26 February 1985 (1985-02-26) cited in the application the whole document	1-18
A	US 4 306 059 A (YOKOBAYASHI KOJI ET AL) 15 December 1981 (1981-12-15) the whole document	1-3
A	US 4 072 567 A (YOKOBAYASHI KOJI ET AL) 7 February 1978 (1978-02-07) the whole document	1-3
P,A	WO 99 40217 A (NEOSE TECHNOLOGIES INC) 12 August 1999 (1999-08-12) the whole document	1-3

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[X] Further documents are listed in the continuation of box C.

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Date of the actual completion of the international search	Date of mailing of the international search report
9 May 2000	18/05/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Tarrida Torrell, J

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 96 06173 A (JACQUES NICHOLAS ANTHONY ;SIMPSON CHRISTINE LYNN (GB); GIFFARD PHI) 29 February 1996 (1996-02-29) page 2, line 13 -page 3, line 20	1-3

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 00/01160

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(74) Agent: BIRCH, Linda, D.; E.I. Du Pont de Nemours and Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).

(81) Designated States: AE, AL, AU, BA, BB, BG, BR, CA, CN, CR, CU, CZ, EE, GD, GE, HR, HU, ID, IL, IN, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, SL, TR, TT, UA, US, UZ, VN, YU, ZA, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

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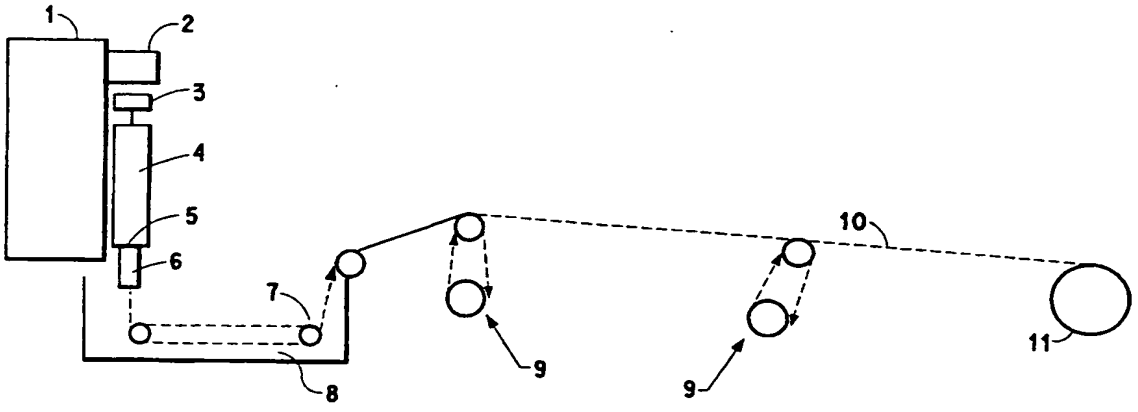
(54) Title: POLYSACCHARIDE FIBERS



(57) Abstract

This invention pertains to novel fibers made of α(1→;3) polysaccharides, and a process for their production. The fibers of the invention have "cotton–like" properties but can be produced as continuous filaments on a year–round basis. The fibers are useful in textile applications.

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TITLE

POLYSACCHARIDE FIBERS

BACKGROUND OF THE INVENTION

This invention pertains to novel fibers made of α(1→3) polysaccharides, and a process for their production. The fibers of the invention have "cotton-like" properties but can be produced as continuous filaments on a year-round basis. The fibers are useful in textile applications.

Polysaccharides have been known since the dawn of civilization, primarily in the form of cellulose, a polymer formed from glucose by natural processes via β(1→4) glucoside linkages; see, for example, Applied Fibre Science, F. Happey, Ed., Chapter 8, E. Atkins, Academic Press, New York, 1979. Numerous other polysaccharide polymers are also disclosed therein.

Only cellulose among the many known polysaccharides has achieved commercial prominence as a fiber as a consequence of the many useful products derived therefrom. In particular, cotton, a highly pure form of naturally occurring cellulose, is well-known for its beneficial attributes in textile applications.

It is further known that cellulose exhibits sufficient chain extension and backbone rigidity in solution to form liquid crystalline solutions; see, for example O'Brien, U.S. Patent 4,501,886. The teachings of the art suggest that sufficient polysaccharide chain extension could be achieved only in β(1→4) linked polysaccharides and that any significant deviation from that backbone geometry would lower the molecular aspect ratio below that required for the formation of an ordered phase.

More recently, glucan polymer characterized by α(1→3) glucoside linkages has been isolated by contacting an aqueous solution of sucrose with GtfJ glucosyltransferase isolated from Streptococcus salivarius, Simpson et al., Microbiology, vol 141, pp. 1451-1460 (1995). Highly crystalline, highly oriented, low molecular weight films of α(1→3)-D-glucan have been fabricated for the purposes of x-ray diffraction analysis, Ogawa et al., Fiber Diffraction Methods, 47, pp. 353-362 (1980). In Ogawa, the insoluble glucan polymer is acetylated, the acetylated glucan dissolved to form a 5% solution in chloroform and the solution cast into a film. The film is then subjected to stretching in glycerine at 150°C which orients the film and stretches it to a length 6.5 times the original length of the solution cast film. After stretching, the film is deacetylated and crystallized by annealing in superheated water at 140°C in a pressure vessel. It is well-known in the art that exposure of polysaccharides to such a hot aqueous environment results in chain cleavage and loss of molecular weight, with concomitant degradation of mechanical properties. Thus, considerable benefit would accrue to a process

which would provide the high orientation and crystallinity desired for fibers without a reduction in molecular weight.

It is highly desirable to discover other polysaccharides having utility as films, fibers or resins because of their widespread importance in the global ecosystem. Polysaccharides based on glucose and glucose itself are particularly important because of their prominent role in photosynthesis and metabolic processes. Cellulose and starch, both based on molecular chains of polyanhydro-glucose are the most abundant polymers on earth and are of great commercial importance. Such polymers offer materials that are environmentally benign throughout their entire life cycle and are constructed from renewable energy and raw materials sources.

The properties exhibited by cellulose and starch are determined by the nature of their enchainment pattern. Hence, starch or amylose consisting of $\alpha(1\rightarrow4)$ linked glucose is not useful for fiber applications because it is swollen or dissolved by water. Alternatively, cellulose, having $\beta(1\rightarrow4)$ enchainment, is a good structural material being both crystalline and hydrophobic, and is commonly used for textile applications as cotton fiber. Like other natural fibers, cotton has evolved under constraints, wherein the polysaccharide structure and physical properties have not been optimized for textile uses. In particular, cotton fiber offers short fiber length, limited variation in cross section and fiber fineness and is produced in a highly labor and land intensive process.

Thus, it is desirable to form new structural polysaccharides through processes such as enzymatic synthesis or through genetic modification of microorganisms or plant hosts and fibers made from such new polysaccharides that retain the desirable features of biodegradability, renewable resource-based feedstocks and low cost.

SUMMARY OF THE INVENTION

The present invention concerns a polysaccharide fiber, comprising: a polymer comprising hexose units wherein at least 50% of the hexose units are linked via an $\alpha(1\rightarrow3)$ glycoside linkage, said polymer having a number average degree of polymerization of at least 100.

The present invention also concerns a process for producing a polysaccharide fiber, comprising the steps of: dissolving a sufficient amount of a polymer comprising hexose units, wherein at least 50% of the hexose units are linked via an $\alpha(1\rightarrow3)$ glycoside linkage, in a solvent or in a mixture comprising a solvent to form a liquid crystalline solution, and spinning a polysaccharide fiber from said liquid crystalline solution.

The present invention further concerns a liquid crystalline solution, comprising: a solvent and an amount sufficient to form liquid crystals of a

polymer comprising hexose units wherein within the polymer at least 50% of the hexose units are linked via an $\alpha(1\rightarrow3)$ glycoside linkage.

BRIEF DESCRIPTION OF THE DRAWINGS

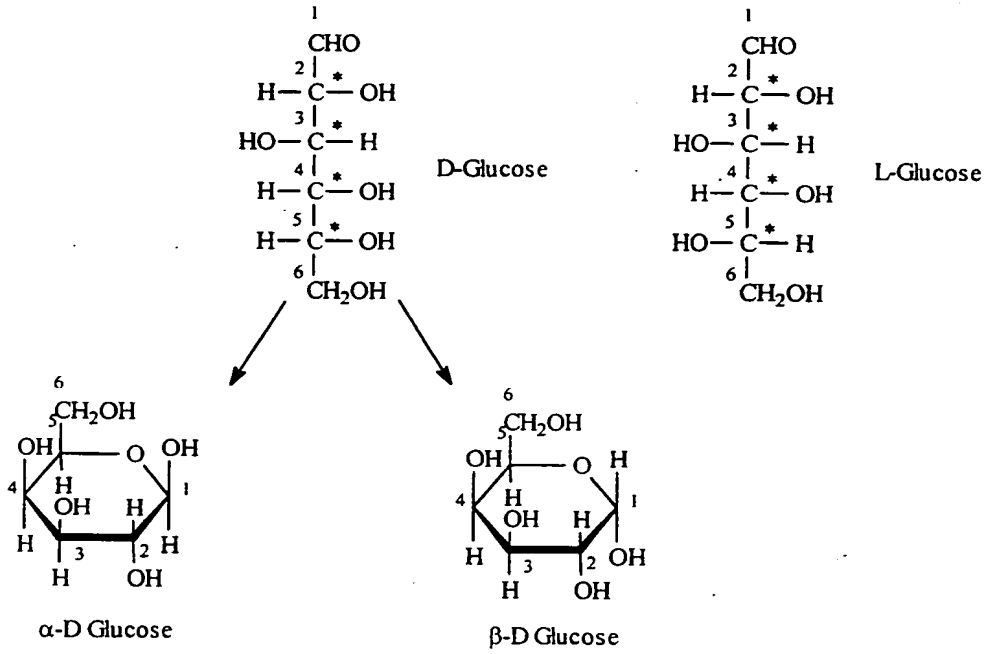
FIG. 1 is a schematic diagram of an apparatus for air gap or wet spinning of liquid crystalline solutions of hexose polymer to form polysaccharide fibers.

DETAILED DESCRIPTION

In one of the surprising aspects of the present invention, it has now been found that a polymer comprising hexose units, wherein at least 50% of the hexose units within the polymer are linked via an $\alpha(1\rightarrow3)$ glycoside linkage, can form a liquid crystalline solution when a sufficient amount of the polymer is dissolved in a solvent or in a mixture comprising a solvent, and that from this solution can be spun a continuous, high strength, cotton-like fiber highly suitable for use in textiles either in a derivatized form, a non-derivatized form or a regenerated form. By "regenerated" is meant that any derivative groups added during the preparation of the fiber are removed.

Suitable for use in the present invention are hexose polymers comprising repeating hexose monomer units wherein at least 50% of the hexose units are linked by an $\alpha(1\rightarrow3)$ glycoside linkage. Such hexose polymers include those formed from the monomers glucose, fructose, mannose, galactose, combinations thereof, and mixtures of any of the foregoing. A linkage involving a glucose monomeric unit can be called a glucoside linkage. Polyhexose polymers used herein include both the dextrorotatory (D) and levorotatory (L) enantiomers of such polymers as well as racemic mixtures thereof. Preferred are the D-forms; most preferred is D-glucose. A racemic mixture is less preferred.

By "$\alpha(1\rightarrow3)$ glycoside linkage" is meant that within the polymer, the repeating monomeric units are linked in a particular manner dictated by an enchainment pattern. The nature of the enchainment pattern depends, in part, on how the ring closes when an aldohexose ring closes to form a hemiacetal. The open chain form of glucose (an aldohexose) has four asymmetric centers (see below). Hence there are 2^4 or 16 possible open chain forms of which D and L glucose are two. When the ring closes, there is a new asymmetric center created at C1 thus making 5 asymmetric carbons. Depending on how the ring closes, for glucose, $\alpha(1\rightarrow4)$-linked polymer, e.g. starch or $\beta(1\rightarrow4)$-linked polymer, e.g. cellulose can be formed upon further condensation to polymer. The configuration at C1 in the polymer determines whether it is an alpha or beta linked polymer, and the numbers in parenthesis following alpha or beta refer to the carbon atoms through which enchainment takes place.



* - asymmetric carbon center

The polymer used to form the polysaccharide fiber of the present invention possesses a number average degree of polymerization of at least 100 and can range up to about 5,000. Preferably, the number average degree of polymerization ranges from about 200 to about 1,000.

The polysaccharides of the present invention can be homoglycans or heteroglycans. If only one type of hexose unit is used during preparation of the polysaccharide, a homoglycan is formed. Glucan is a homoglycan formed from glucose. If more than one type of hexose unit is used, a heteroglycan is formed.

The polymer of the polysaccharide fibers of the present invention can further comprise monomer units other than hexose units, such as pentoses. It is preferred that substantially all of the monomer units within the polymer in the present invention are hexose monomer units. By "substantially all" is meant at least 90%.

In a similar vein, the polysaccharide fibers of the present invention can further comprise monomer units linked by a glycoside linkage other than α(1→3), such as α(1→4), α(1→6), β(1→2), β(1→3), β(1→4) or β(1→6) or any combination thereof. At least 50% of the glycoside linkages in the polymer are an α(1→3) glycoside linkage. Preferably, substantially all of the linkages are α(1→3) glycoside linkages, and most preferably all of the hexose units in the polymer are linked by an α(1→3) glycoside linkage. By "substantially all" is meant at least 90%.

The polysaccharide fibers of the present invention are produced by dissolving the polymer, described above, in a solvent or in a mixture comprising a solvent, to form a liquid crystalline solution. Oriented fiber is then spun from the liquid crystalline solution.

The isolation and purification of various polysaccharides is described in, for example, The Polysaccharides, G. O. Aspinall, Vol. 1, Chap. 2, Academic Press, New York, 1983. In a preferred embodiment of the present invention, poly(α(1→3)-D-glucose) is formed by contacting an aqueous solution of sucrose with GtfJ glucosyltransferase isolated from Streptococcus salivarius according to the methods taught in the art. Any method which results in a purity of ca. 90% or greater is satisfactory. One such method is provided in detail hereinbelow.

The polymer comprising hexose units can be derivatized, preferably acetylated, most preferably close to 100% acetylated, in order to facilitate rendering the polysaccharide soluble in the spinning solvent to achieve a solids level sufficient for liquid crystals to form. For examples of representative polysaccharide derivatives useful herein, see The Polysaccharides, G. O. Aspinall, Vol. 2, Chap. 2, Academic Press, New York, 1983. Preferred derivatives include methyl, ethyl, hydroxyethyl, nitrate, acetate, proprionate and butyrate. A preferred derivatized polymer is a poly(α(1→3)-D-glucose acetate). Acetylation can be accomplished using the method described by O'Brien, op.cit., for acetylating cellulose. It can be useful to pre-activate the hexose polymer by first contacting it with acetic acid prior to its contact with an acetylation mixture such as a mixture of glacial acetic acid, acetic anhydride, and methylene chloride. Contact with the mixture is followed by the addition of perchloric acid to initiate esterification.

Following optional formation of the derivative, the polymer is dissolved in a solvent or in a mixture comprising a solvent to form a liquid crystalline solution. By "liquid crystalline solution" is meant a solution in which a spontaneous phase separation from randomly dispersed polymer molecules to domains of locally ordered molecules has occurred. Formation of the liquid crystalline solution is dependent on the solids content of the polymer so dissolved. "Solids content" refers to the amount of dry polymer before it is dissolved. It is calculated as the (wt. of polymer)/(wt. of polymer + wt. of solvent). A liquid crystalline solution must be formed in order to obtain an oriented fiber when the solution is spun. The amount of polymer needed to provide a solids content sufficient for liquid crystals to form depends on the polymer morphology and the polymer molecular weight. The onset of liquid crystallinity can be determined by an observable increase in the birefrigence of the solution being formed. Birefringence can be determined by any convenient means as are known in the art.

Non-derivatized polymers and the derivatized polymers formed as described above are soluble in solvents including organic halides, organic acids, fluorinated alcohols, or mixtures thereof. Representative of such solvents are methylene chloride (dichloromethane), trifluoroacetic acid, trichloroacetic acid, dichloroacetic acid, formic acid, hexafluoroisopropanol, and mixtures such as trifluoroacetic acid/methylene chloride, trichloroacetic acid/methylene chloride, dichloroacetic acid/methylene chloride, and formic acid/methylene chloride. Other suitable solvents include molecules which are nonsolvents by themselves (e.g., water) in combination with strong organic acids, such as trifluoroacetic acid/water, trichloroacetic acid/water, dichloroacetic acid/water, or formic acid/water. Preferably, an acetylated polymer is dissolved in a mixture of trifluoroacetic acid and methylene chloride, most preferably as a 60/40 v/v. mixture of trifluoroacetic acid and methylene chloride, respectively, at a temperature between about 0 and about 25°C while mixing, preferably mixing under high shear.

The particular benefits of the present invention are achieved by virtue of the formation of the liquid crystalline solution comprising a solvent and an amount sufficient to form liquid crystals of a polymer comprising hexose units wherein at least 50% of the hexose units are linked via an $\alpha(1\rightarrow3)$glycoside linkage from which a highly oriented, highly crystalline continuous filament can be drawn. A preferred liquid crystalline solution is one wherein substantially all of the hexose units are linked via an $\alpha(1\rightarrow3)$glycoside linkage. A preferred polymer for a liquid crystalline solution is poly($\alpha(1\rightarrow3)$-D-glucose acetate). One of skill in the art will understand that the minimum polymer concentration (solids content) required for achieving the formation of the liquid crystalline phase will vary according to the specific molecular morphology and the molecular weight of the polymer. A liquid crystalline solution having a solids content of at least 10% is preferred. A solids content ranging from about 10% to about 35% is more preferred herein, and most preferred is about 20 to about 35%. In a preferred embodiment of the present invention, it has been found that the minimum polymer concentration for phase separation of 100% poly($\alpha(1\rightarrow3)$-D-glucose) is ca. 15% by weight in a 60/40 mixture of trifluoroacetic acid and methylene chloride when the number average molecular weight of the polymer is ca. 60,000 Daltons. Optimum spinning performance for this particular polymer is achieved at about 20 to about 30% by weight solids content, which is most preferred.

Spinning from the liquid crystalline solution can be accomplished by means known in the art, and as described in O'Brien, op.cit. The viscous spinning solution can be forced by means such as the push of a piston or the action of a pump through a single or multi-holed spinneret or other form of die. The

spinneret can be of any cross-sectional shape, including round, flat, multi-lobal, and the like, as are known in the art. The extruded strand can then be passed by ordinary means into a coagulation bath wherein is contained a liquid which dissolves the solvent of the spinning solvent but not the polymer thereof, thus causing the highly oriented polymer to coagulate into a fiber according to the present invention.

Under some circumstances, a superior result is achieved when the extruded strand first passes through an inert, noncoagulating layer, usually an air gap, prior to introduction into the coagulation bath. When the inert layer is an air gap, the spinning process is known as air-gap spinning. Under other circumstances, extrusion directly into the coagulation bath is preferred, known as wet-spinning. Preferred solvents for the coagulation bath include aliphatic alcohols, particularly methanol, ethanol, or isopropanol.

FIG. 1 is a schematic diagram of an apparatus for wet or air-gap spinning of polysaccharide fibers. Syringe pump 1 drives ram 2 at a controlled rate onto piston 3 of spinning cell 4. A suitable syringe pump is a Harvard model 44. Spinning cell 4 can contain a metal filter, such as a Dynalloy® X5, 10 μm sintered metal filter, above spinneret 6. Extrudate 12 is optionally directed through an inert non-coagulating layer and into liquid coagulating bath 8 and directed back and forth between guides 7 which, for example, can be ceramic or comprise Teflon® fluoropolymer. On exiting the coagulation bath, the extrudate can be optionally directed through a drawing zone between two independently driven rolls 9 and collected on bobbins, preferably stainless steel, at wind-up 11.

If in a derivatized form, the polysaccharide fibers of the present invention can be retained in such derivatized form. However, it is preferred to regenerate such fibers by converting them back to the hydroxyl reconstituted form. This can be accomplished by numerous means known in the art, such as by contacting the polysaccharide fiber with an excess of a saponification or hydrolysis medium. One deacetylation means found to be satisfactory herein is base-catalyzed saponification. For example, the acetylated fiber can be contacted with 0.05 molar methanolic sodium methoxide, or with a dilute aqueous base solution, such as 5% aqueous sodium or potassium hydroxide, for 24-72 hours at room temperature, to remove ester groups, such as the acetyl group.

It is quite surprising that poly(α(1→3)-D-glucose) forms liquid crystalline solutions, and that the highly desirable fibers of the present invention can be spun therefrom. Likewise for other polyhexoses comprising at least 50% α(1→3) glycoside linkages in combination with other non preferred linkages, liquid crystalline behavior can be observed. For example, Nigeran which includes α(1→3) and α(1→4) glycoside linkages can be dissolved in a solvent to form a

liquid crystalline solution. However, other α-linked polyglucoses, especially those containing substantially all α(1→6) or α(1→4) linkages, and more generally other α-linked polysaccharides do not exhibit similar behavior, for example amylose (starch) which has α(1→4) linkages, dextran with α(1→6) linkages, and pullulan with α(1→4) and α(1→6) linkages.

The white, lustrous fibers of the present invention are characterized by a tensile strength of at least 1 gram per denier, preferably 2 grams per denier.

EXAMPLES

POLYMER ISOLATION

In the examples following, except Example 7, two batches of poly(α(1→3)-D-glucose) were employed, designated P1 and P2.

P1 was produced according to the following sequence. The mature peptide encoded by the gtf-J gene of Streptococcus salivarius (strain ATCC 25975) was cloned by PCR amplification of template DNA from Streptococcus salivarius using primers based on the gene sequence described in Genbank accession number Z11873 and by Giggard et al., J. Gen. Microbiol. 137 (Pt 11), 2577-2593 (1991).

PCR reactions were run using the 5' primer SEQ ID NO:1:

5'-GGGAATTCCATATGAACATTGATGGTAAATATTAC

where SEQ ID NO:2, the sequence:

AACATTGATGGTAAATATTAC

corresponds to bases 555 through 547 of Genbank accession number Z11873 and the remaining 5' bases provide an Nde I recognition site and a few 5' bases to allow digestion of the PCR product with Nde I.

The 3' primer SEQ ID NO:3 had the sequence (read 5' to 3')

5'-AGATCTAGTCTTAGTTTAGCACTCTAGGTGG

where SEQ ID NO:4 the sequence:

TTAGTTTAGCACTCTAGGTGG

corresponds to the reverse compliment of bases 4559 through 4580 in Genbank accession number Z11873 and the remaining bases provide an Xba I site and extra bases to allow digestion of the PCR product with Xba I.

The PCR product was digested with Nde I and Xba I then purified by agarose gel electrophoresis and isolated. The fragment was ligated into the *E. coli* protein expression vector pET24a (Novagen) that had been digested with Nde I and Nhe I. The ligation reaction was used to transform *E. coli* cell line DH10B, and six clonal colonies from that transformation were grown and plasmid DNA was isolated. The plasmid DNA from each of these lines was used to transform *E. coli* cell line DE3.

Single colonies from each transformation were grown overnight in rich media, the resultant culture was diluted to about 0.05 optical density units at

600 nm and then re-grown to 2 optical density units at 600 nm then protein expression from the pET24a plasmid was induced by the addition of 1 mM isopropylthiogalactoside. Cells were harvested by centrifugation after 3 hr, re-suspended in 50 mM KPO_4 buffer at pH 6 which also contained 0.2 mM phenylmethylsulfonyl fluoride and disrupted by sonication.

Clonal cultures producing active dextran sucrase were identified by adding 10 ml of the cell extract to 50 mM sucrose and 0.5 mg ml-1 T-10 dextran (Sigma) in a total reaction volume of 100 ml of 50 mM KPO_4 buffer. Active clones producing enzyme polymerize glucose using sucrose as the glucosyl donor and producing insoluble polymer thus clouding the reaction solution within about 10 minutes. The polymer was lyophilized to form a dry powder.

P2 was produced in a larger scale modification of the process for producing P1. Production of the crude enzyme was done by scaling the procedure employed for the production of P1 to two one-liter cultures in shake flasks. Isolated cells were disrupted by French Press disruption using the buffer system described above. The cell extract was diluted to 10 mg of protein ml-1, brought to 30% saturation with ammonium sulfate and centrifuged to remove a small amount of precipitate. The supernatant was brought to 70% saturation in ammonium sulfate and the precipitated protein isolated by centrifugation. The protein pellet was stored as a suspension in 70% saturated ammonium sulfate and used as the suspension.

Poly ($\alpha(1\rightarrow3)$-D-glucose) was produced by adding the ammonium sulfate suspension to a 2 l solution of 200 mM sucrose in 50 mM KPO_4 buffer pH 6 and stirring overnight at 28°C. The insoluble glucose polymer produced was removed from solution by centrifugation, re-suspended in water (500 ml) and again centrifuged. The water wash was repeated two more times and the centrifuge pellet was concentrated by vacuum filtration on a sintered glass filter. The filter cake was stored at 4°C prior to use.

TESTING METHODS

Physical properties such as tenacity, elongation and initial modulus were measured using methods and instruments conforming to ASTM Standard D 2101-82, except that the test specimen length was one inch. Reported results are averages for 3 to 5 individual filament tests.

EXAMPLE 1

2.86 g of wet polymer P2 was boiled in 150 ml deionized water for 1 h. After cooling, the product was collected by filtration and washed 3X with glacial acetic acid. The polymer, still wet with acetic acid, was suspended in a prechilled (-25°C) acetylating mixture consisting of acetic anhydride (20 ml), glacial acetic acid (14 ml) and methylene chloride (20 ml). Mechanical stirring was started and

70% aqueous perchloric acid (0.2 ml) was added to initiate esterification. The reaction mixture was allowed to warm to 0°C and held there for 3 h. The reaction mixture was subsequently allowed to warm to room temperature and held for 1 h, then frozen in dry ice overnight, and then warmed to room temperature again.

The viscous, homogeneous solution of thus acetylated P2 polymer was precipitated in methanol with rapid stirring and collected by filtration. The filtrate was thoroughly washed twice with methanol, then five times with deionized water, and then four times with methanol. The washed product was collected by filtration and allowed to air dry yielding 1.78 g of purified acetylated polymer which was soluble in methylene chloride. Size exclusion chromatography in hexafluoroisopropanol containing 0.1M sodium triflate was conducted through two Showdex 80M columns yielding relative molecular weight values of M_n=60,800 and M_w=202,300.

1.5 g of the thus prepared $\alpha(1\rightarrow3)$ glucan acetate was combined with 2.79 g of a solvent mixture consisting of 100 parts by weight trifluoroacetic acid (99%) and 8 parts by weight deionized water to form a 35% solids solution. In order to dissolve the polymer therein, the mixture of polymer and solvent was first stirred by hand using a stainless steel spatula in order to homogenize the mixture. The homogenized mixture was then pumped back and forth between two syringes connected by a short length of 3 mm ID stainless steel tubing. Dissolution of the polymer in the solvent mixture was complete within 4 h at room temperature. The solution was examined microscopically through crossed polarizers and found to be highly birefringent, confirming an oriented, lyotropic liquid crystalline phase.

The liquid crystalline solution so formed was transferred into a vertically positioned polyethylene syringe fitted with a Dynalloy® X5 sintered stainless steel filter available from Fluid Dynamics/Memtec Group, Deland, Fl. Trapped air was allowed to migrate to the top of syringe and vented during installation of the syringe plunger. This assembly was then fitted to a vertically mounted Harvard model 55-1144 syringe pump for controlled rate extrusion according to the parameters given in Table 1. The syringe was fitted with a stainless steel single hole spinneret having a hole diameter of .005 inches and capillary length of .010 inches. The face of the spinneret was maintained 0.5 inches above the surface of the methanol coagulation bath. The filament was extruded at 20 ft/min, drawn into the bath and directed around ceramic guides at both ends of the coagulation tray to obtain a total travel in the bath of 14 feet. (See Figure 1) The coagulated fiber, still wet with methanol, was wound onto stainless steel bobbins at 58 ft/min. The bobbins were soaked in methanol overnight and the filaments were allowed to air dry before mechanical testing. As spun filament

tenacity/elongation/modulus values were 4.2/17.5/53.9 grams per denier/percent/grams per denier, respectively.

EXAMPLE 2

The as-spun fiber of Example 1 was deacetylated to yield regenerated poly ($\alpha(1\rightarrow3)$-D-glucose) fibers with good mechanical properties. A small skein of the fiber of Example 1 was immersed in a large excess of 0.05M methanolic sodium methoxide and allowed to stand at room temperature for 24-72 h under nitrogen. The skein was removed, washed with methanol, blotted and air dried. Filament tenacity/elongation/modulus values were 2.7/12.5/51.3 grams per denier/percent/grams per denier, respectively.

EXAMPLE 3

1.0 g of dried powder of P1 polymer was suspended in deionized water and boiled under nitrogen for 2 h. After cooling, the powder was collected by filtration and pressed to yield a wet filter cake. This was subsequently immersed in 100 ml of glacial acetic acid, stirred for 5 minutes at room temperature and collected by filtration. The acetic acid rinse was repeated and the powder was collected and pressed to remove excess acetic acid.

The filter cake was then added to a chilled (-25°C) acetylation medium consisting of acetic anhydride (10 ml, 99.7%), glacial acetic acid (7 ml) and dichloromethane (10 ml). Perchloric acid (0.1 ml, 70%) was added and the reaction maintained with stirring at a temperature in the range of -30°C to -2°C for 6 h and then allowed to warm to 24°C and held for 30 min. The resulting viscous mixture was precipitated into rapidly stirred methanol and then filtered. The filter cake was then washed once with methanol, followed by two washings with deionized water and then once with acetone. After drying, the yield was 1.2 g of purified acetylated polymer in the form of an off-white flake.

1 g of the thus prepared acetylated polymer was suspended in 3 g of a 60%/40% by volume mixture of trifluoroacetic acid (99%) and dichloromethane. After the polymer was dispersed in the solvent, the solution was mixed as described in Example 1. The resulting solution was lyotropic and highly fiber forming. The thus formed liquid crystalline solution was transferred to a polyethylene syringe fitted with a filter and extruded using the same general procedure as for Example 1. The filament was extruded at 10.4 fpm through a 0.5 inch air gap into methanol (bath length = 13 ft) and wound up at 36 ft/min. As-spun filament tenacity/elongation/modulus values were 1.6/11.7/34.5 grams per denier/percent/grams per denier, respectively.

EXAMPLE 4

A 6" skein of the as-spun filament of Example 3 was prepared from 5 wraps of continuous filament and the ends were tied together. A 50 g weight

was suspended from the bottom of the skein (consisting of 10 total filaments) and the assembly was immersed in a large excess of 0.05m methanolic sodium methoxide and maintained under nitrogen for 96 h. The filament was removed, washed by immersion in fresh methanol and allowed to air dry. The thus regenerated or deacetylated filament tenacity/elongation/modulus values were 2.4/13.0/52.2 grams per denier/percent/grams per denier, respectively.

EXAMPLE 5

Poly (α(1→3)-D-glucose) acetate fibers were prepared as described in Example 3, except that the wind-up speed was 23 ft/min and the coagulation bath temperature was 3°C. As-spun filament tenacity/elongation/modulus values were 1.9/14.2/32.7 grams per denier/percent/grams per denier, respectively.

EXAMPLE 6

Polymer P1 (2.0 g) was added as a dried powder to a chilled (0°C) mixture of glacial acetal acid (99%, 14 ml), acetic anhydride (99.7%, 10 ml) and dichloromethane (20 ml). The reactants were kept under nitrogen and a catalyst solution at 0°C of perchloric acid (70% aqueous, 0.2 ml) in acetic anhydride (10 ml) was added dropwise with rapid stirring. After addition of the catalyst solution, the reactants were allowed to warm to room temperature and stirred for 5 h. The amber-colored viscous solution thus formed was precipitated into methanol. The filter cake was washed twice with methanol, collected by filtration and vacuum dried at 50°C to yield 2.65 (g) of off-white polymer flake.

1.0 g of the thus acetylated polymer was dissolved in trifluoroacetic acid/dichloromethane (60/40 v/v, 4.0 g) and mixed using the method of Example 1. The resulting solution was lyotropic and fiber forming. Extrusion was carried out using the general procedures described in Example 1, and the specific conditions in Table 1 below, except that it was wet-spun. As-spun filament tenacity/elongation/modulus values were 0.94/14.4/23.1 grams per denier/percent/grams per denier, respectively.

EXAMPLE 7

Nigeran (an alternating α(1→3), α(1→4) glucan), 0.86g (from Asperigillus japonicus, Cat #N2888, Sigma - Aldrich Co.) was suspended in 50 ml of glacial acetic acid for 20 min and collected by filtration. This step was repeated once more and the starting material (still wet with acetic acid) was added to a three necked flask containing the acetylation medium prechilled to 2°C and fitted with a thermocouple, stirrer and nitrogen inlet tube. The acetylation medium consisted of acetic anhydride (20 ml), glacial acetic acid (14 ml) and methylene chloride (20 ml). Perchloric acid, (0.2 ml, 70% aqueous) was then added dropwise with rapid stirring while maintaining the temperature between 2-5°C. The reaction was maintained at this temperature for 3h and subsequently allowed

to warm to room temperature for an additional 3h. The acetylated polymer was then isolated by precipitation into methanol, and collected by filtration. Additional washings with methanol (2 times) were conducted yielding 0.96g of a white product.

A 30% solids solution of the above polymer in trifluoroacetic acid/water (100/8 w/w) was prepared and observed to be birefringent when viewed through crossed polarizing filters verifying the existence of a liquid crystalline solution.

COMPARATIVE EXAMPLE 1

0.5 g of the purified acetylated polymer of Example 6 was dissolved in trifluoroacetic acid/dichloromethane (60/40 v/v, 2.8 g) using the method of Example 1. The resulting solution was not lyotropic (a liquid crystalline solution did not form) because the solids content was below the critical concentration for liquid crystalline phase separation, and was poorly fiber forming. Filament extrusion was carried out as described for Example 4 and the specific conditions in Table 1. As-spun fibers were soaked in methanol for 24 h before being dried and tested. As-spun filament tenacity/elongation/modulus values were 0.54/17.2/17.4 grams per denier/percent/grams per denier, respectively.

COMPARATIVE EXAMPLE 2

A skein of the as-spun filament of Comparative Example 1 was deacetylated in .05 m methanolic sodium methoxide using the procedure described in Example 2. Filament tenacity/elongation/modulus values were 0.4/2.5/25.1 grams per denier/percent/grams per denier, respectively. Thus, regeneration of the poorly oriented isotropically spun precursor fiber gave a poor fiber.

COMPARATIVE EXAMPLE 3

Preparation of Debranched Amylose

$\alpha(1\rightarrow6)$ branch points were enzymatically removed from common corn starch as follows. 300 g of corn starch was gelatinized by heating in 8 L of water at 100°C for 1 hour. The gelatinized starch was cooled to 50°C and 50 ml of 1 M acetic acid was added to adjust the pH to about 4. 1 million units of isoamylase (Sigma) were added in 25 ml of sodium acetate buffer (50 mM, pH 4.5) and the mixture was incubated at 45°C for 4 hours.

1.2 L of butanol was added to the above reaction mixture, and the mix was boiled for 1 hour. The mixture was then allowed to cool to room temperature slowly overnight. The mixture was further cooled to 5°C and the precipitate was collected by centrifugation (GS-3 Rotor, 9500 rpm, 30 minutes). The collected precipitate was resuspended in 8 L water, boiled for 30 minutes and precipitated a second time as above. After centrifugation the precipitate was washed with ethanol and dried overnight at 50°C. Gel Permeation Chromatography (GPC) was

used to compare the resulting product with debranched starch before precipitation verifying removal of the short amylopectin branches.

Preparation of poly(α(1→4)-D-glucose)acetate (Polymer D)

Enzymatically debranched amylose from cornstarch (5.0 g), α(1→4)-D-glucose, was suspended in 100 ml water and boiled for 1 h under nitrogen. On cooling, the suspension was cooled to 0°C and the swollen starch granules were collected by filtration. The wet filter cake was washed 4X with glacial acetic on the filter and the acid-exchanged filter cake was pressed to remove excess acetic acid. This was added to a reaction flask equipped with a paddle stirrer and charged with acetic anhydride (99.7%, 200 ml), acetic acid (99%, 70 ml) and dichloromethane (100 ml), all prechilled to 2°C. Perchloric acid (70% aqueous, 0.5 ml) was added dropwise while maintaining an ice bath around the reaction vessel. After 2 h the reaction mixture was clear and was precipitated by pouring into rapidly stirred methanol. The white product was washed twice in methanol and dried in vacuum at 50°C. The yield was 6.5 g of poly (α(1→4)-D-glucose acetate) which was readily soluble in dichloromethane and mixtures of trifluoroacetic acid with dichloromethane or water.

A 1.0 g portion of the thus acetylated polymer was dissolved in dichloromethane (4.0 g). The viscous solution was not liquid crystalline as evidenced by the absence of birefringence when viewed through crossed polarizers. The fiber forming solution was extruded using the general procedures for Example 1 and the specific parameters in Table 1. The extrudate was not sufficiently strong to allow for several passages through the coagulation bath and best spinning continuity was observed without the use of an air gap. As-spun filament tenacity/elongation/modules values were 0.5/70.6/13.9 grams per denier/percent/grams per denier, respectively.

COMPARATIVE EXAMPLE 4

1.5 g of the acetylated poly (α(1→4)-D-glucose) of Comparative Example 3 was dissolved in a mixture of trifluoroacetic acid and water (4.5 g) 100/8 w/w to provide a 25% solids solution. The resulting spin dope was not liquid crystalline as evidenced by the absence of birefringence when viewed through crossed polarizers. The solution was transferred to a 5 ml syringe fitted with a scintered metal filter and extruded through 0.25 inch air gap using the general procedures of Example 1 and the specific parameters in Table 1. As in Comparative Example 2, the spinning threadline was not sufficiently strong to allow multiple passes in the coagulation bath. The as-spun fiber exhibited a dull appearance and measured filament tenacity/elongation/modulus values were 0.3/14.7/12.6 grams per denier/percent/grams per denier, respectively.

TABLE 1

Source	Polymer	Solvent	Polymer Concen. % Solids	Dia Holes (in.)	Hole L/d	Pump Rate Ml/min	Jet Vel Fpm	Length (ft)	Temp (°c)	Airgap (in.)	Speed (fpm)	S.S.F.*
											WIND-UP	
Ex. 1	α(1-3) glucan acetate	TFA/H_2O 100/8 w/w	35	0.005	2	0.08	20	14	-1	0.5	58	2.9
Ex. 2	α(1-3) glucan	SAPONIFIED										
Ex. 3	α(1-3) glucan acetate	TFA/CH_2Cl_2 60/40 v/v	25	0.005	2	0.04	10.36	13	9	0.5	36	3.5
Ex. 4	α(1-3) glucan	SAPONIFIED UNDER TENSION										
Ex. 5	α(1-3) glucan acetate	TFA/CH_2Cl_2 60/40 v/v	25	0.005	2	0.04	10.36	13	3	0.5	23	2.2
Ex. 6	α(1-3) glucan acetate	TFA/CH_2Cl_2 60/40 v/v	20	0.005	5	0.08	20.72	5	17	0	29	1.4
Comp. Ex. 1	α(1-3) glucan acetate	TFA/CH_2Cl_2 60/40 v/v	15	0.005	4	0.08	20.72	5	18	0	15	0.7
Comp. Ex. 2	α(1-3) glucan	SAPONIFIED										
Comp. Ex. 3	α(1-4) glucan acetate	CH_2Cl_2	20	0.005	2	0.08	20	0.91	23	0	15	0.7
Comp. Ex. 4	α(1-4) glucan acetate	TFA/H_2O 100/8 w/w	25	0.005	4	0.08	5	1.08	20	0.25	48	2.4

*Spin Stretch Factor

WHAT IS CLAIMED IS:

1. A polysaccharide fiber, comprising: a polymer comprising hexose units wherein at least 50% of the hexose units are linked via an α(1→3) glycoside linkage, said polymer having a number average degree of polymerization of at least 100.

2. The polysaccharide fiber of Claim 1 wherein substantially all of the hexose units are linked via an α(1→3) glycoside linkage.

3. The polysaccharide fiber of Claim 1 wherein the polymer is poly(α(1→3)-D-glucose.

4. The polysaccharide fiber of Claim 1 wherein the fiber has a tensile strength of at least 1 gram per denier.

5. A process for producing a polysaccharide fiber, comprising the steps of: dissolving a sufficient amount of a polymer comprising hexose units wherein at least 50% of the hexose units are linked via an α(1→3) glycoside linkage in a solvent or in a mixture comprising a solvent to form a liquid crystalline solution; and spinning a polysaccharide fiber from said liquid crystalline solution.

6. The process of Claim 5 wherein substantially all of the hexose units are linked via an α(1→3) glycoside linkage.

7. The process of Claim 6 wherein prior to dissolving, the polymer is derivatized.

8. The process of Claim 7 wherein the polymer is acetylated.

9. The process of Claim 8 wherein the derivatized polymer is a poly(α(1→3)-D-glucose acetate).

10. The process of Claim 8 further comprising contacting the polysaccharide fiber with an excess of a saponification or hydrolysis medium to form a regenerated polysaccharide fiber.

11. The process of Claim 5 wherein the solvent is selected from the group consisting of: an organic acid, an organic halide, a fluorinated alcohol, and mixtures thereof.

12. The process of Claim 5 wherein the solution has a solids content of at least 10%.

13. The process of Claim 12 wherein the solids content ranges from about 20 to about 35%.

14. A liquid crystalline solution, comprising: a solvent and an amount sufficient to form liquid crystals of a polymer comprising hexose units wherein at least 50% of the hexose units are linked via an α(1→3) glycoside linkage.

15. The liquid crystalline solution of Claim 14 wherein substantially all of the hexose units are linked via an α(1→3) glycoside linkage.

16. The liquid crystalline solution of Claim 14 wherein the polymer is poly(α(1→3)-D-glucose acetate).

17. The liquid crystalline solution of Claim 14 wherein the solvent is selected from the group consisting of: an organic acid, an organic halide, a fluorinated alcohol, and any combination thereof.

18. The liquid crystalline solution of Claim 14 wherein the amount of polymer provides a solids content of at least 10%.

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PCT/US00/01160

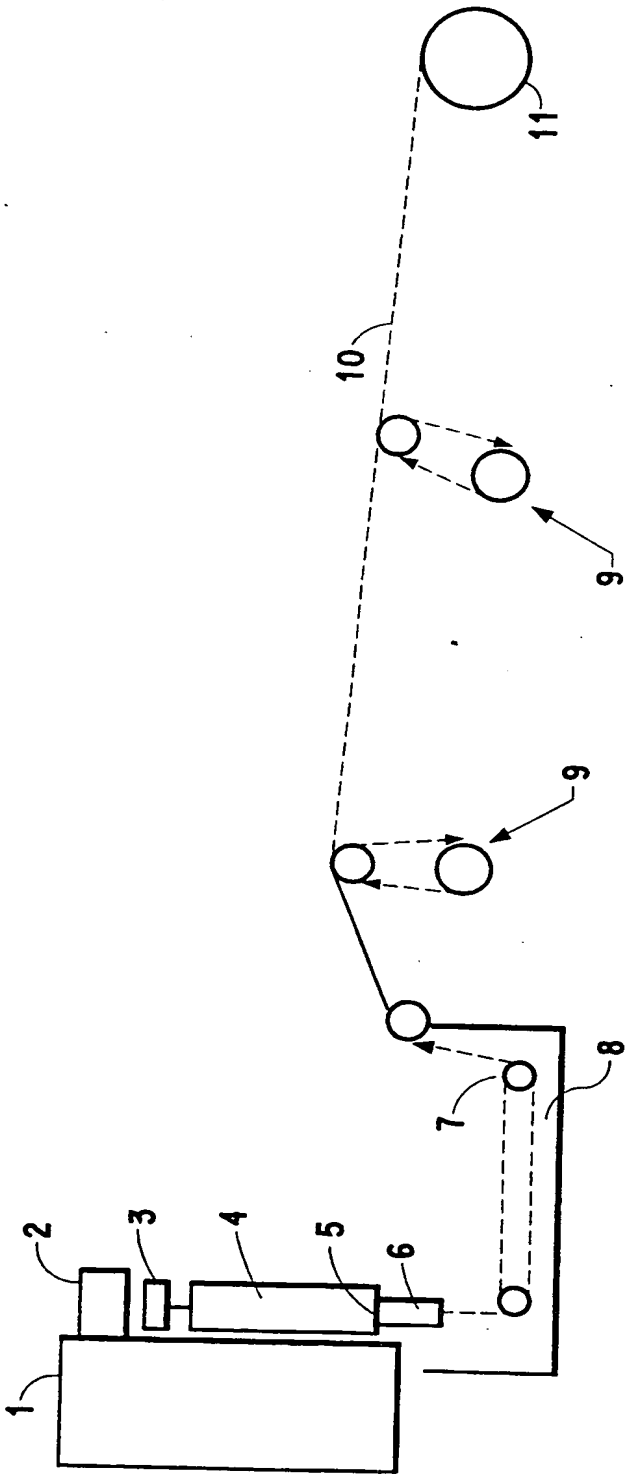

FIG. 1

09/857572
JC[redacted]c'd PCT/PTO 05 JUN 2001
PCT/US00/01160

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/01160

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 D01F9/00 C08L5/00 C12P19/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 D01F C08L C12P

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 501 886 A (O'BRIEN JOHN P) 26 February 1985 (1985-02-26) cited in the application the whole document	1-18
A	US 4 306 059 A (YOKOBAYASHI KOJI ET AL) 15 December 1981 (1981-12-15) the whole document	1-3
A	US 4 072 567 A (YOKOBAYASHI KOJI ET AL) 7 February 1978 (1978-02-07) the whole document	1-3
P,A	WO 99 40217 A (NEOSE TECHNOLOGIES INC) 12 August 1999 (1999-08-12) the whole document	1-3

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
9 May 2000	18/05/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Tarrida Torrell, J

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/01160

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	WO 96 06173 A (JACQUES NICHOLAS ANTHONY ;SIMPSON CHRISTINE LYNN (GB); GIFFARD PHI) 29 February 1996 (1996-02-29) page 2, line 13 -page 3, line 20	1-3

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter. Application No
PCT/US 00/01160

Patent document cited in search report	Publication dat	Patent family member(s)	Publication date
US 4501886 A	26-02-1985	US 4464323 A	07-08-1984
		CA 1203959 A	06-05-1986
		DE 3378983 D	23-02-1989
		EP 0103398 A	21-03-1984
		JP 1709320 C	11-11-1992
		JP 3077284 B	10-12-1991
		JP 59047417 A	17-03-1984
		KR 8802094 B	15-10-1988
		SU 1565350 A	15-05-1990
US 4306059 A	15-12-1981	JP 1337448 C	29-09-1986
		JP 54052793 A	25-04-1979
		JP 60054322 B	29-11-1985
		DE 2842855 A	12-04-1979
		FR 2404655 A	27-04-1979
		GB 2007245 A,B	16-05-1979
US 4072567 A	07-02-1978	JP 1157425 C	25-07-1983
		JP 52117492 A	01-10-1977
		JP 57045558 B	28-09-1982
		CA 1085329 A	09-09-1980
		GB 1521810 A	16-08-1978
WO 9940217 A	12-08-1999	US 5952205 A	14-09-1999
		AU 2566199 A	23-08-1999
		EP 0973931 A	26-01-2000
WO 9606173 A	29-02-1996	AU 702520 B	25-02-1999
		AU 3248295 A	14-03-1996
		CA 2198281 A	29-02-1996
		EP 0777735 A	11-06-1997
		NZ 291364 A	29-03-1999
		US 5981838 A	09-11-1999

PATENT COOPERATION TREAT

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JUN 0 5 2000
LDB
TECH CENTER 1600/2900

From the INTERNATIONAL SEARCHING AUTHORITY

PCT

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL SEARCH REPORT OR THE DECLARATION

(PCT Rule 44.1)

To:
E.I. DU PONT DE NEMOURS AND COMPANY
Legal/Patent Records Center
Attn. Birch, Linda D.
1007 Market Street
Wilmington, Delaware 19898
UNITED STATES OF AMERICA

RECEIVED
MAY 25 2000
PATENT RECORDS CENTER

√cc: CRD

RECEIVED
OCT 03 2001

	Date of mailing *(day/month/year)* 18/05/2000
Applicant's or agent's file reference CL1330PCT	**FOR FURTHER ACTION** See paragraphs 1 and 4 below
International application No. PCT/US 00/01160	International filing date *(day/month/year)* 19/01/2000
Applicant E.I. DU PONT DE NEMOURS AND COMPANY	

1. [X] The applicant is hereby notified that the International Search Report has been established and is transmitted herewith.

Filing of amendments and statement under Article 19:
The applicant is entitled, if he so wishes, to amend the claims of the International Application (see Rule 46):

When? The time limit for filing such amendments is normally 2 months from the date of transmittal of the International Search Report; however, for more details, see the notes on the accompanying sheet.

Where? Directly to the International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland
Fascimile No.: (41-22) 740.14.35

For more detailed instructions, see the notes on the accompanying sheet.

2. [ ] The applicant is hereby notified that no International Search Report will be established and that the declaration under Article 17(2)(a) to that effect is transmitted herewith.

3. [ ] **With regard to the protest** against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:

[ ] the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.

[ ] no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

4. **Further action(s):** The applicant is reminded of the following:

Shortly after **18 months** from the priority date, the international application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in Rules 90*bis*.1 and 90*bis*.3, respectively, before the completion of the technical preparations for international publication.

Within **19 months** from the priority date, a demand for international preliminary examination must be filed if the applicant wishes to postpon the ntry into th national phase until 30 months from th priority dat (in som Offices even later).

Within **20 months** from th priority date, th applicant must perform the prescribed acts for entry into the national phase before all designated Offices which hav not been lected in the demand or in a later election within 19 months from the priority date or could not be elected because they are not bound by Chapter II.

Nam and mailing address of the International Searching Authority European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 po nl, Fax: (+31-70) 340-3016	Authorized officer Alicja Van der Heijden

CLS NOTED
6.5.2000
MISG

NOTES TO FORM PCT/ISA/220

These Notes are intended to give the basic instructions concerning the filing of amendments under article 19. The Notes are based on the requirements of the Patent Cooperation Treaty, the Regulations and the Administrative Instructions under that Treaty. In case of discrepancy between these Notes and those requirements, the latter are applicable. For more detailed information, see also the PCT Applicant's Guide, a publication of WIPO.

In these Notes, "Article", "Rule", and "Section" refer to the provisions of the PCT, the PCT Regulations and the PCT Administrative Instructions respectively.

INSTRUCTIONS CONCERNING AMENDMENTS UNDER ARTICLE 19

The applicant has, after having received the international search report, one opportunity to amend the claims of the international application. It should however be emphasized that, since all parts of the international application (claims, description and drawings) may be amended during the international preliminary examination procedure, there is usually no need to file amendments of the claims under Article 19 except where, e.g. the applicant wants the latter to be published for the purposes of provisional protection or has another reason for amending the claims before international publication. Furthermore, it should be emphasized that provisional protection is available in some States only.

What parts of the international application may be amended?

Under Article 19, only the claims may be amended.

During the international phase, the claims may also be amended (or further amended) under Article 34 before the International Preliminary Examining Authority. The description and drawings may only be amended under Article 34 before the International Examining Authority.

Upon entry into the national phase, all parts of the international application may be amended under Article 28 or, where applicable, Article 41.

When?

Within 2 months from the date of transmittal of the international search report or 16 months from the priority date, whichever time limit expires later. It should be noted, however, that the amendments will be considered as having been received on time if they are received by the International Bureau after the expiration of the applicable time limit but before the completion of the technical preparations for international publication (Rule 46.1).

Where not to file the amendments?

The amendments may only be filed with the International Bureau and not with the receiving Office or the International Searching Authority (Rule 46.2).

Where a demand for international preliminary examination has been/is filed, see below.

How?

Either by cancelling one or more entire claims, by adding one or more new claims or by amending the text of one or more of the claims as filed.

A replacement sheet must be submitted for each sheet of the claims which, on account of an amendment or amendments, differs from the sheet originally filed.

All the claims appearing on a replacement sheet must be numbered in Arabic numerals. Where a claim is cancelled, no renumbering of the other claims is required. In all cases where claims are renumbered, they must be renumbered consecutively (Administrative Instructions, Section 205(b)).

The amendments must be made in the language in which the international application is to be published.

What documents must/may accompany the amendments?

Letter (Section 205(b)):

The amendments must be submitted with a letter.

The letter will not be published with the international application and the amended claims. It should not be confused with the "Statement under Article 19(1)" (see below, under "Statement under Article 19(1)").

The letter must be in English or French, at the choice of the applicant. However, if the language of the international application is English, the letter must be in English; if the language of the international application is French, the letter must be in French.

The letter must indicate the differences between the claims as filed and the claims as amended. It must, in particular, indicate, in connection with each claim appearing in the international application (it being understood that identical indications concerning several claims may be grouped),whether

(i) the claim is unchanged;

(ii) the claim is cancelled;

(iii) the claim is new;

(iv) the claim replaces one or more claims as filed;

(v) the claim is the result of the division of a claim as filed.

The following examples illustrate the manner in which amendments must be explained in the accompanying letter:

1. [Where originally there were 48 claims and after amendment of some claims there are 51]:
"Claims 1 to 29, 31, 32, 34, 35, 37 to 48 replaced by amended claims bearing the same numbers; claims 30, 33 and 36 unchanged; new claims 49 to 51 added."

2. [Where originally there were 15 claims and after amendment of all claims there are 11]:
"Claims 1 to 15 replaced by amended claims 1 to 11."

3. [Where originally there were 14 claims and the amendments consist in cancelling some claims and in adding new claims]:
"Claims 1 to 6 and 14 unchanged; claims 7 to 13 cancelled; new claims 15, 16 and 17 added." or
"Claims 7 to 13 cancelled; new claims 15, 16 and 17 added; all other claims unchanged."

4. [Where various kinds of amendments are made]:
"Claims 1-10 unchanged; claims 11 to 13, 18 and 19 cancelled; claims 14, 15 and 16 replaced by amended claim 14; claim 17 subdivided into amended claims 15, 16 and 17; new claims 20 and 21 added."

"Statement under article 19(1)" (Rule 46.4)

The amendments may be accompanied by a statement explaining the amendments and indicating any impact that such amendments might have on the description and the drawings (which cannot be amended under Article 19(1)).

The statement will be published with the international application and the amended claims.

It must be in the language in which the international appplication is to be published.

It must be brief, not exceeding 500 words if in English or if translated into English.

It should not be confused with and does not replace the letter indicating the differences between the claims as filed and as amended. It must be filed on a separate sheet and must be identified as such by a heading, preferably by using the words "Statement under Article 19(1)."

It may not contain any disparaging comments on the international search report or the relevance of citations contained in that report. Reference to citations, relevant to a given claim, contained in the international search report may be made only in connection with an amendment of that claim.

Consequence if a demand for international preliminary examination has already been filed

If, at the time of filing any amendments under Article 19, a demand for international preliminary examination has already been submitted, the applicant must preferably, at the same time of filing the amendments with the International Bureau, also file a copy of such amendments with the International Preliminary Examining Authority (see Rule 62.2(a), first sentence).

Consequence with regard to translation of the international application for entry into the national phase

The applicant's attention is drawn to the fact that, where upon entry into the national phase, a translation of the claims as amended under Article 19 may have to be furnished to the designated/elected Offices, instead of, or in addition to, the translation of the claims as filed.

For further details on the requirements of each designated/elected Office, see Volume II of the PCT Applicant's Guide.

PATENT COOPERATION TREAT

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference	**FOR FURTHER ACTION**	see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.
CL1330PCT		
International application No.	International filing date *(day/month/year)*	(Earliest) Priority Date *(day/month/year)*
PCT/US 00/ 01160	19/01/2000	25/01/1999
Applicant		
E.I. DU PONT DE NEMOURS AND COMPANY		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 03 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**

   a. With regard to the **language,** the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

   [ ] the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

   b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

   [ ] contained in the international application in written form.

   [ ] filed together with the international application in computer readable form.

   [ ] furnished subsequently to this Authority in written form.

   [ ] furnished subsequently to this Authority in computer readble form.

   [ ] the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

   [ ] the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. [ ] **Certain claims were found unsearchable** (See Box I).

3. [ ] **Unity of Invention is lacking** (see Box II).

4. With regard to the **title,**

   [X] the text is approved as submitted by the applicant.

   [ ] the text has been established by this Authority to read as follows:

5. With regard to the **abstract,**

   [X] th t xt is approved as submitted by the applicant.

   [ ] th text has been established, according to Rul 38.2(b), by this Authority as it appears in Box III. The applicant may, within on month from the date of mailing f this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with th abstract is Figure No. 1

   [X] as suggested by the applicant.

   [ ] None of the figures.

   [ ] because th applicant failed to suggest a figure.

   [ ] because this figure better characterizes the invention.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/01160

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 D01F9/00 C08L5/00 C12P19/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 D01F C08L C12P

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 501 886 A (O'BRIEN JOHN P) 26 February 1985 (1985-02-26) cited in the application the whole document	1-18
A	US 4 306 059 A (YOKOBAYASHI KOJI ET AL) 15 December 1981 (1981-12-15) the whole document	1-3
A	US 4 072 567 A (YOKOBAYASHI KOJI ET AL) 7 February 1978 (1978-02-07) the whole document	1-3
P,A	WO 99 40217 A (NEOSE TECHNOLOGIES INC) 12 August 1999 (1999-08-12) the whole document	1-3

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
9 May 2000	18/05/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Tarrida Torrell, J

Form PCT/ISA/210 (second sheet) (July 1992)

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 96 06173 A (JACQUES NICHOLAS ANTHONY ;SIMPSON CHRISTINE LYNN (GB); GIFFARD PHI) 29 February 1996 (1996-02-29) page 2, line 13 -page 3, line 20	1-3

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 00/01160

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4501886 A	26-02-1985	US 4464323 A	07-08-1984
		CA 1203959 A	06-05-1986
		DE 3378983 D	23-02-1989
		EP 0103398 A	21-03-1984
		JP 1709320 C	11-11-1992
		JP 3077284 B	10-12-1991
		JP 59047417 A	17-03-1984
		KR 8802094 B	15-10-1988
		SU 1565350 A	15-05-1990
US 4306059 A	15-12-1981	JP 1337448 C	29-09-1986
		JP 54052793 A	25-04-1979
		JP 60054322 B	29-11-1985
		DE 2842855 A	12-04-1979
		FR 2404655 A	27-04-1979
		GB 2007245 A,B	16-05-1979
US 4072567 A	07-02-1978	JP 1157425 C	25-07-1983
		JP 52117492 A	01-10-1977
		JP 57045558 B	28-09-1982
		CA 1085329 A	09-09-1980
		GB 1521810 A	16-08-1978
WO 9940217 A	12-08-1999	US 5952205 A	14-09-1999
		AU 2566199 A	23-08-1999
		EP 0973931 A	26-01-2000
WO 9606173 A	29-02-1996	AU 702520 B	25-02-1999
		AU 3248295 A	14-03-1996
		CA 2198281 A	29-02-1996
		EP 0777735 A	11-06-1997
		NZ 291364 A	29-03-1999
		US 5981838 A	09-11-1999

PATENT COOPERATION TREATY

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NOV 03 2000
PATENT RECORDS CENTER

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

Birch, Linda D.
E.I. DU PONT DE NEMOURS AND COMPANY
Legal/Patent Records Center
1007 Market Street
Wilmington, Delaware 19898
ETATS-UNIS D'AMERIQUE

DT/PCT Rec'd 05 JUN2001

PCT

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Rule 71.1)

Date of mailing *(day/month/year)*	30.10.2000
Applicant's or agent's file reference CL1330PCT	**IMPORTANT NOTIFICATION**

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US00/01160	19/01/2000	25/01/1999

Applicant
E.I. DU PONT DE NEMOURS AND COMPANY

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.

2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.

3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. **REMINDER**

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of th PCT Applicant's Guide.

TRB NOTED

Name and mailing address of the IPEA/	Authorized officer
European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Aperribay, I Tel.+49 89 2399-8154

Form PCT/IPEA/416 (July 1992)

25 JUL 2001

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
CL1330PCT		
International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US00/01160	19/01/2000	25/01/1999
International Patent Classification (IPC) or national classification and IPC D01F9/00		
Applicant E.I. DU PONT DE NEMOURS AND COMPANY		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 6 sheets, including this cover sheet.

   ☐ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the report
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations suporting such statement
   - VI ☐ Certain documents cited
   - VII ☐ Certain defects in the international application
   - VIII ☒ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
27/07/2000	30.10.2000
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Contet, F Telephone No. +49 89 2399 8671

Form PCT/IPEA/409 (cover sheet) (January 1994)

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/US00/01160

I. Basis f the r port

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

Description, pages:

1-15 as originally filed

Claims, No.:

1-18 as originally filed

Drawings, sheets:

1/1 as originally filed

2. The amendments have resulted in the cancellation of:

☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims 1-18
	No:	Claims
Inventive step (IS)	Yes:	Claims 1-18
	No:	Claims
Industrial applicability (IA)	Yes:	Claims 1-18
	No:	Claims

2. Citations and explanations

see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

Re Item V

Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Reference is made to the following documents:

D1 : US-A-4 306 059 (YOKOBAYASHI KOJI ET AL) 15 December 1981
D2 : US-A-4 501 886 (Dupont, O'BRIEN JOHN P) 26 February 1985

I- Novelty :

The present application is concerned with a process for preparing polysaccharide fibres having the desired mechanical properties and able to withstand hot aqueous environment without a reduction in molecular weight.
Thus a polymer comprising hexose units, wherein at least 50% of the hexose units are linked via an α(1→3) glycoside linkage is dissolved in a solvent or a solvents mixture and the liquid crystalline solution obtained is then spun. The filaments are suitable in the textile field.

Both D1 and D2 solve the same problem of providing fibres from renewable material.
1- D1, Claims 1 and 2, discloses fibres made from Elsinan, an alpha-glucan having a molecular weight of 10000 to 10^7 and the structural hexose units linked through α(1→3)- and α(1→4) glycoside linkages (col. 2, line 43-52), wherein the main structure is approximately three α-1,4 linked-glucose residues repeatedly linked in α-1,3 fashion (Col.2, lines 63-65).
Elsinan is water-soluble, but insoluble in organic solvents such as methanol, ethanol, chloroform, acetone or ethyl acetate.

Fibres can be obtained by spinning an aqueous solution of Elsinan. The filaments thus obtained are suitable for making medicinal or sanitary goods and paper (Ex.5).

2- D2 discloses the obtention of fibres from cellulosic material having properties approaching those of aramid fibres. Thus cellulose triacetate having a β(1→4)

glycoside linkage is dissolved in a solvent mixture trifluoroacetic acid/ methylene chloride or trifluoroacetic acid/formic acid and spun. The filaments obtained are useful in ropes and cordage.

3- The subject-matter claimed differs in that the polysaccharide used has at least 50% of the hexose units in the polysaccharide linked via an α(1→3) glycoside linkage.

Therefore, novelty of the subject-matter claimed can be acknowledged over the available prior art.

II- Inventive step:

The problem to be solved by the present invention may therefore be regarded as to provide further polysaccharide fibres having good mechanical properties and which do not show reduction in molecular weight when submitted to a heat treatment (p.1, l.38 - p.2, l.2).

On the one hand, the structure of the polymer is different from the one used in D2 and on the other hand, the properties of the polymer and of fibres obtained according to the present invention are respectively different from those according to D1.

Thus, the choice of the polysaccharide of Claim 1 in order to solve the problem posed was not suggested in this available prior art taken alone or in combination.

Thus, the subject-matter claimed can be deemed to be inventive over the available prior art.

III- Industrial applicability:

To provide fibres from renewable material having suitable mechanical properties.

Re Item VIII

Certain observations on the international application

- Claim 2: The term "substantially " used in this claim is vague and unclear. As a matter of fact it has been defined on page 4, lines 24, 25 (" at least [illegible] use in Claim 2 leaves the reader in doubt as to the meaning of the technical

feature to which it refers, thereby rendering the definition of the subject-matter of said claim unclear (Article 6 PCT).

- **Claim 4:** This Claim should include the method of measurement of the tensile strength or at least a reference to the description.

- **Claim 13:** Your attention is drawn to the word "about". Its presence especially in ranges prevents the scope of protection to be clearly defined.

- The embodiment of the invention described on pages 2, line 3 and lines 22-26 does not fall within the scope of the claims (Article 6 PCT). Since these polysaccharides are already known (US-A-4 072 567), they can only be considered as representing background art useful for understanding the invention (see the PCT Guidelines, III-4.3).